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THERMODYNAMIC PROPERTIES OF THE Nb-I SYSTEM

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Equilibrium vapor pressures of Nb-I system were measured by using the Broudon's gauge at temperatures between 293 and 1050 K. Considering the main gaseous species of the Nb-I system at high temperatures, the standard Gibbs' energy functions, $\Delta G^\circ = -21.0 \times 10^3 + 10.1\,T$ ($T = 850 - 1000$ K), were calculated for the following reaction from both the partial pressures and material balance; $Nb\ (s) + 2\ I_2\ (g) \rightleftharpoons NbI_4\ (g)$.

A knowledge regarding the thermodynamics in the Nb-I system is important for the preparation of the single crystal of Nb-S or Nb-Se compounds using iodine as a transporting agent as well as for the purification of metallic niobium. However, there are no reports on thermodynamics in the Nb-I system. In this study, the Broudon's gauge was used to measure the equilibrium pressure on the Nb-I system at temperatures between 293 and 1050 K, and a thermodynamic consideration has been made for the resulting reaction; $Nb(s) + 2I_2(g) \rightleftharpoons NbI_4(g)$.

The equilibrium pressures were measured by the following procedure using the apparatus described in Ref. 1. The empty Broudon's gauge was heated to 1173 K and evacuated (about 10^{-4} Torr) for 3 h. A sample mixture (niobium metal powder and iodine; $Nb = 4.63 \times 10^{-5}$ mol and $I_2 = 1.28 \times 10^{-4}$ mol, I/Nb = 5.51) was sealed in a quartz capillary and put into the recooled gauge. The entire system was then degassed under vacuum for several hours and sealed. The sealed apparatus was put into the furnace, and the pressure was measured at various temperatures with continuous heating.

The total pressure - temperature relationship is shown in Fig. 1. The range indicated as (a) shows the evaporation process of the solid iodine and the range indicated as (b) shows the thermal expansion of the I_2 gas. The gaseous I_2 neither react with metallic niobium nor dissociate to I(g) (less than 0.08% at 663 K) at temperature below 663 K. This is supported by the fact that the ideal gas law holds good in this region because the extrapolation of the line of the pressure down to the lower temperatures reaches to 0 K (shown in Fig. 1). At 663 K, the total pressure decreases suddenly indicating the initiation of some reaction between iodine and niobium (discussed later). In the region of temperature from 668 to 873 K shown by the solid circle in Fig. 1, the measured pressure might not represent the equilibrium one because of the reaction rate of iodine and niobium is very slow in this temperature region compared with the heating rate (0.5 K/min). In the region of the temperature from 873 to 1050 K, the pressure increases due to the dissociation of iodine ($I_2 \rightleftharpoons 2I$) in addition to the usual thermal expansion.

By extrapolating of P-T curve ((c) in Fig. 1) approximated by the exponential curve, $P = A\exp(BT)$, the actual equilibrium total pressure at 663 K is calculated to be 0.28 atm. The gaseous species of the Nb-I system for the reaction of iodine and niobium are thought to be NbI_2, NbI_3, NbI_4, and NbI_5. If it is supposed that all the niobium metal reacts with the I_2 gas, then the total pressure owing to the formation of NbI_n are estimated to be 0.428 ($n = 2$), 0.349 ($n = 3$), 0.272 ($n = 4$), and 0.192 ($n = 5$), respectively. The value of the actual equilibrium total pressure equal to 0.28 atm at 663 K is very close to that of the formation of NbI_4 (0.272 atm). The existence of NbI_4(g) is also supported by Refs. 1 and 2

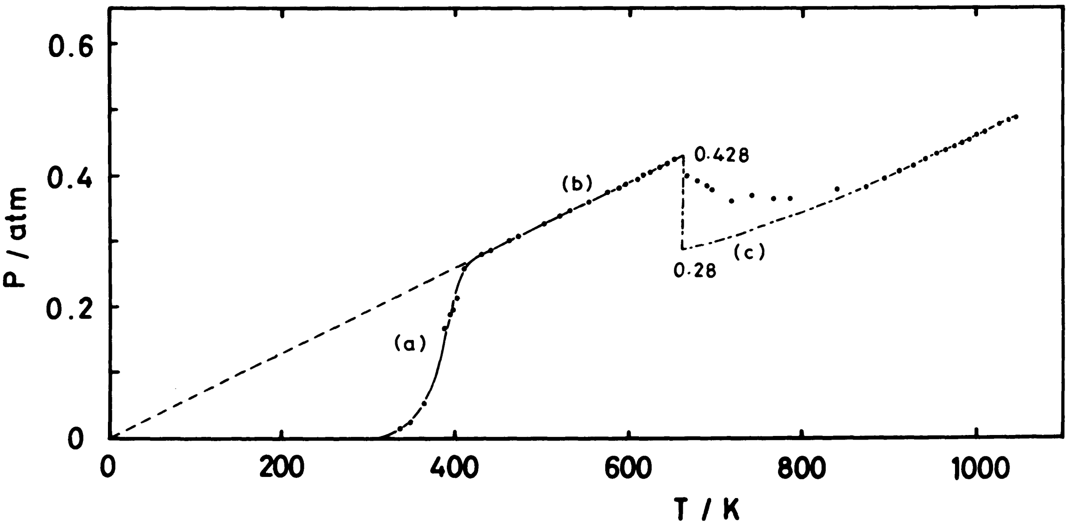

Fig. 1. Pressure versus temperature curve for the Nb-I system.

concerning the presence of other transition metal iodide as $TiI_4(g)$ and $VI_4(g)$, respectively. On the basis of the above discussion, $NbI_4(g)$, $I_2(g)$, and $I(g)$ are considered to be the predominant gaseous species in the Nb-I system at high temperature, and complete reactions in this system are thought to be as follows;

$$Nb(s) + 2\,I_2(g) \rightleftharpoons NbI_4(g) \qquad (1)$$

$$I_2(g) \rightleftharpoons 2\,I(g) \qquad (2)$$

Accordingly, the total pressure, P, is expressed as

$$P = P_I + P_{I_2} + P_{NbI_4} \qquad (3)$$

where P_I, P_{I_2}, and P_{NbI_4} represent the partial pressure of I, I_2, and NbI_4, respectively. From the material balance for iodine, the following equation

$$n^\circ_I = \frac{V}{R\,T}\,(\,P_I + 2\,P_{I_2} + 4\,P_{NbI_4}\,) \qquad (4)$$

is derived, where n°_I is initial amount of iodine and V is the volume calculated as 16.3 cm^3 from the relation of P and T in the region (b). The value of n°_I is known (2.55×10^{-4} mol) and the ratio of P_I^2 / P_{I_2} is calculated from Eq. 2 using the thermodynamic data[3]. From Eq. 3, Eq. 4, and the ratio of P_I^2 / P_{I_2}, each partial pressure at high temperatures has been calculated. Using these values of partial pressures, both equilibrium constant K_p and the standard Gibbs' free energy, ΔG°, for Eq. 1 have been calculated. All these calculated values are listed in Table 1. By using the relation $\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$, ΔH° and ΔS° of Eq. 1 have also been calculated. The plots of ΔG° against T are shown in Fig. 2. In the temperature region higher than about 1000 K, the plots deviated from the straight line. In this region, the measured pressure values were lower than that predicted because of the difficulty of the keeping the whole system at homogeneous temperature. The ΔH° is calculated from the slope of the van't Hoff plots. The evaluated thermodynamic functions for Eq. 1 are as follows;

$$\Delta H^\circ / J\ mol^{-1} = -\ 21.0 \times 10^3$$

$$\Delta S^\circ / J\ mol^{-1}\ K^{-1} = -\ 10.1$$

$$\Delta G^\circ / J\ mol^{-1} = -\ 21.0 \times 10^3 + 10.1\ T$$

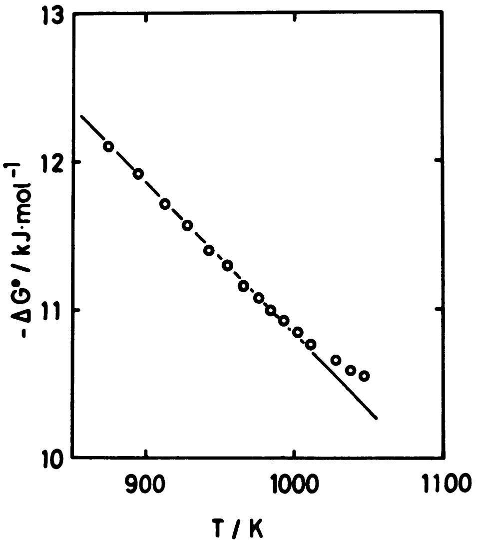

Fig. 2. Plots of ΔG° versus temperature for the reaction of $Nb(s) + 2I_2(g) \rightleftharpoons NbI_4(g)$.

Table 1. Partial pressures of I, I_2, and NbI_4, and calculated values of $\Delta G°$ for the reaction of $Nb(s) + 2\ I_2(g) \rightleftharpoons NbI_4(g)$.

T / K	P / atm	K_p*	P_I / atm	P_{I_2} / atm	P_{NbI_4} / atm	K_p	$-\Delta G°$ / kJ mol^{-1}
875	0.378	2.125×10^{-4}	0.006	0.188	0.186	5.29	12.1
895	0.391	3.409×10^{-4}	0.008	0.195	0.188	4.97	11.9
913	0.402	5.125×10^{-4}	0.010	0.202	0.190	4.68	11.7
928	0.411	7.112×10^{-4}	0.012	0.207	0.192	4.48	11.6
943	0.420	9.767×10^{-4}	0.014	0.212	0.193	4.28	11.4
955	0.428	1.250×10^{-3}	0.016	0.217	0.195	4.15	11.3
966	0.435	1.558×10^{-3}	0.019	0.221	0.196	4.02	11.2
976	0.441	1.896×10^{-3}	0.021	0.224	0.197	3.92	11.1
984	0.447	2.212×10^{-3}	0.022	0.227	0.197	3.84	11.0
993	0.453	2.624×10^{-3}	0.025	0.230	0.198	3.76	10.9
1002	0.459	3.102×10^{-3}	0.027	0.233	0.199	3.68	10.9
1011	0.465	3.658×10^{-3}	0.029	0.236	0.200	3.60	10.8
1028	0.477	4.955×10^{-3}	0.035	0.241	0.202	3.48	10.7
1038	0.484	5.896×10^{-3}	0.038	0.244	0.202	3.41	10.6
1047	0.490	6.875×10^{-3}	0.041	0.246	0.203	3.36	10.6

K_p* ($I_2 \rightarrow 2I$) : from JANAF thermochemical tables

K_p ($Nb + 2I_2 \rightarrow NbI_4$)

References

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3) JANAF thermochemical tables, Natl. Stand. Ref. Data Ser., NBS, 2nd ed , 1971 (U.S. National Bureau of Standards, Washington DC).

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